

# Direct observation of charge density wave order at zero magnetic field in ortho-II $\text{YBa}_2\text{Cu}_3\text{O}_{6.54}$

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X-ray diffraction measurements show that the high-temperature superconductor  $\text{YBa}_2\text{Cu}_3\text{O}_{6.54}$ , with ortho-II oxygen order, has charge density wave order (CDW) in the absence of an applied magnetic field. The CDW has a  $1\text{-}\mathbf{q}$  structure with the in-plane component of the wavevector parallel to the  $\mathbf{b}$ -axis (chain direction), with a similar incommensurability to that observed in ortho-VIII and ortho-III samples, which have different dopings and oxygen orderings. Our results for ortho-II contrast with recent high-field NMR measurements, which suggest a commensurate wavevector along the  $\mathbf{a}$ -axis. We discuss the relationship between spin and charge correlations in  $\text{YBa}_2\text{Cu}_3\text{O}_y$ , and recent high-field quantum oscillation, NMR and ultrasound experiments.

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Charge density waves (CDWs) have recently been observed in the high temperature superconductors (HTS)  $\text{YBa}_2\text{Cu}_3\text{O}_y$  (YBCO) and  $(\text{Y}/\text{Nd})\text{Ba}_2\text{Cu}_3\text{O}_y$  [1–3]. The CDW, that competes with HTS, develops in a region inside the celebrated pseudogap phase, where a number of other probes, including high-field NMR [4], the Kerr effect [5], and the Hall effect [6], show signatures of electronic ordering. This last effect is smoothly connected to the low-temperature high-field quantum oscillations (QO) [7] that demonstrated the existence of small Fermi surface (FS) pockets.

The existence of ground states with competing order is central to many theories of HTS. A widely discussed example is “stripe order”, that is a state with coexisting charge and spin order [8]. Stripe order is observed in some HTS and related compounds, such as  $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$  [9] and  $\text{La}_{1.6-x}\text{Nd}_{0.4}\text{Sr}_x\text{CuO}_4$  [10]. It is important to establish whether the tendency towards stripes is a generic property of the cuprates and whether the spin and charge correlations are always related.

$\text{YBa}_2\text{Cu}_3\text{O}_y$  differs from, e.g.  $\text{La}_{2-x}(\text{Ba},\text{Sr})_x\text{CuO}_4$ , in that it contains bilayers of  $\text{CuO}_2$  planes, separated by layers containing a certain fraction (depending on  $y$ ) of  $\text{Cu-O}$  chains. The oxygen-filled chains, which run along the orthorhombic crystal  $\mathbf{b}$ -direction tend to order and are labelled ortho- $N$ , depending on the repeat length ( $Na$ ) of the ordering of the chains along  $\mathbf{a}$  [11]. A major gap in the CDW picture to date was the failure to observe a CDW in the ortho-II state (the most highly ordered, having alternating full and empty  $\text{Cu-O}$  chains). This

was surprising because many studies of this composition had suggested that such order is present, at least in high field [4, 6, 12–15]. Recently, ultrasound measurements have indicated a  $2\text{-}\mathbf{q}$  state in high magnetic fields [16].

In this Letter, we report the observation of a CDW in an ortho-II sample of  $\text{YBa}_2\text{Cu}_3\text{O}_{6.54}$  in zero magnetic field. The CDW has a  $1\text{-}\mathbf{q}$  structure, with wave vector  $\mathbf{q}_{\text{CDW}} = (0, 0.329(2), 0.5)$ . This contrasts with both lower and higher dopings, where a  $2\text{-}\mathbf{q}$  structure is reported [1–3]. Both the wavevector magnitude and direction differ from those inferred from NMR measurements in high field [4]. The propagation vectors of the charge and spin correlations in ortho-II YBCO do not appear to follow the simple relationship  $\delta_{\text{charge}} = 2\delta_{\text{spin}}$  observed in stripe systems [9, 10]. We examine the doping dependence of the CDW order in high quality ortho-II, -III and -VIII samples (hereafter denoted o-II, o-III and o-VIII).

We carried out high energy (100 keV) X-ray diffraction experiments on three  $\sim 99\%$  detwinned  $\text{YBa}_2\text{Cu}_3\text{O}_y$  single crystals (sample characteristics are given in Table. 1). These samples have orthorhombic crystal structures ( $a \approx 3.82$  (ignoring the chain-ordering superlattices),  $b \approx 3.87$  and  $c \approx 11.7$  Å). Samples were mounted in a closed-cycle cryostat on a 4-circle diffractometer on beamline BW5 at the DORIS storage ring (DESY). This allowed access to a wide range of reciprocal space ( $h, k, \ell$ ) expressed in units of  $(2\pi/a, 2\pi/b, 2\pi/c)$ , at temperatures down to 6 K.

A CDW modulation with characteristic wavevector  $\mathbf{q}_{\text{CDW}}$  gives rise to satellites around reciprocal lattice

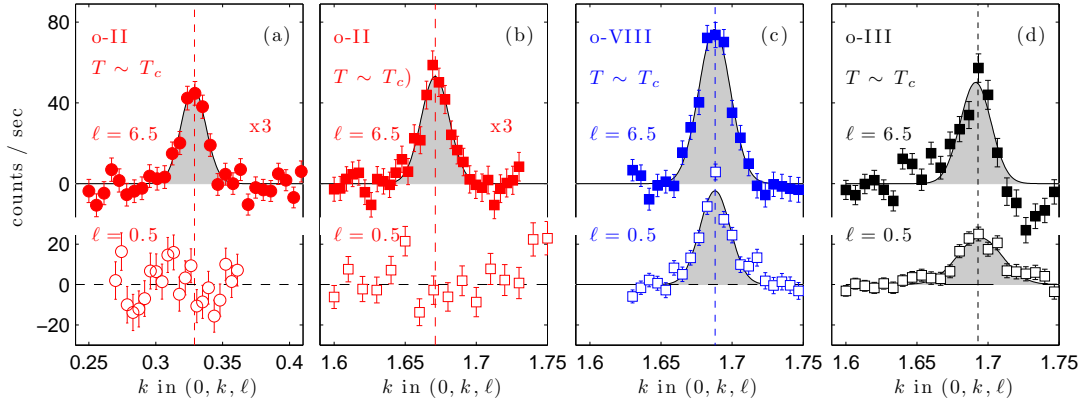


FIG. 1:  $k$ -scans through the CDW wavevector positions  $(0, \delta_2, \ell)$  and  $(0, 2 - \delta_2, \ell)$  in YBCO o-II, -VIII, and -III at  $T \sim T_c$ . (a, b) For o-II,  $\delta_2 = 0.329(2)$  incommensurate peaks are only observed at  $\ell = 6.5$ , suggesting a strong CDW displacement along  $z$ . (c, d) For o-VIII and o-III, peaks are observed at  $\ell = 0.5$  and  $6.5$  with  $\delta_2 = 0.313(2)$  and  $0.305(2)$  respectively. Linear backgrounds have been subtracted in panels (a) and (b). To avoid contamination from weakly  $T$ -dependent spurious peaks in (c) and the o-III superlattice peak from the minority domain in (d), we plot  $I(T_c) - I(140\text{ K})$  corrected for a sloping background as in (a, b). Intensities in (a, b) have been multiplied by a factor 3 to compensate for the smaller o-II sample size.

$y$ in YBCO	Oxygen ordering	Doping level $p$	$T_c$ (K)	$T_{\text{CDW}}$ (K)	$\delta_1$ (a) (r.l.u)	$\delta_2$ (b) (r.l.u)
6.54	o-II	0.104	58	155(10)	-	0.329(2)
6.67	o-VIII	0.123	67	140(10)	0.305(2)	0.313(2)
6.75	o-III	0.132	74	140(10)	0.30 [3]	0.304(2)

TABLE I: Characteristics of the  $\text{YBa}_2\text{Cu}_3\text{O}_y$  samples studied. The superconducting  $T_c$  was determined from the 1 Oe field-cooled magnetization and doping was evaluated from Ref. 17.  $T_{\text{CDW}}$ ,  $\delta_1$  and  $\delta_2$  are derived from our high energy X-ray experiments (quoted uncertainties in the values of  $\delta$  are dominated by minor crystal alignment errors) and from Ref. 3.

points at positions  $\mathbf{Q} = \boldsymbol{\tau} \pm \mathbf{q}_{\text{CDW}}$ . High energy X-ray diffraction is sensitive to the atomic displacements parallel to the scattering vector  $\mathbf{Q}$  [2]. Our previous measurements [2] on o-VIII showed  $\mathbf{q}_{\text{CDW}} = (\delta_1, 0, 0.5)$  and  $(0, \delta_2, 0.5)$  (see Table 1). Fig. 1(a,b) shows  $k$ -scans performed on YBCO o-II through the positions  $(0, \delta, \ell)$  and  $(0, 2 - \delta, \ell)$ , with  $\ell = 0.5, 6.5$  and  $\delta \sim 0.3$ . No CDW peaks were found at  $\ell = 0.5$ , but well-defined peaks were observed at  $\ell = 6.5$ . These peaks constitute the first direct X-ray evidence for CDW order in YBCO o-II and indicate that the displacements are mainly polarised along  $\mathbf{c}$ . For comparison,  $k$ -scans through the positions  $(0, 2 - \delta, \ell)$  in o-VIII and o-III are shown in Fig. 1(c, d) for  $\ell = 0.5$  and  $6.5$ ; again, for modulations along  $k$ , the signal at  $\ell = 6.5$  is stronger.

In YBCO o-VIII and -III, a lattice modulation is found along both the  $\mathbf{a}$ - and  $\mathbf{b}$ -axis directions [1–3]. For o-II, we have searched for a CDW along the  $\mathbf{a}$ -axis, concentrating on positions where a signal was observed in o-VIII. Wavevectors  $(|n - \delta|, 0, \ell)$  with  $n = 2, 4$  for  $\ell = 0.5$  and

$n = 0, 2, 4$  for  $\ell = 6.5$  were measured and no signal from a lattice modulation was found above the noise level (see Fig. 2(a, b)). To this accuracy, a modulation along the  $\mathbf{a}$ -axis with  $\ell$  half-integral is ruled out.

Even though the CDW structures in YBCO o-II, -III and -VIII are different, the signals from the  $\mathbf{b}$ -axis modulation have very similar dependence on  $\ell$ ,  $T$  and magnetic field. Fig. 3(a) shows the  $\ell$ -dependence near  $\ell = 6.5$  at  $T \sim T_c$ . All three compounds have a broad peak at  $\ell \approx 6.5$ , with a width corresponding to a correlation length of  $\xi_c \lesssim 10\text{ \AA}$ . The  $T$ -dependence of several reflections is plotted in Fig. 3(c). As was previously shown for YBCO o-VIII and o-III [1–3], the intensity grows below an onset temperature  $T_{\text{CDW}}$  ( $\sim 140\text{ K}$ ) down to the respective  $T_c$ 's, below which a partial suppression takes place. Here we show a similar behaviour in o-II, but with a slightly higher onset temperature. The application of a magnetic field enhances the low- $T$  intensity in a similar fashion to that reported in YBCO o-VIII [2].

Modelling of our  $\mathbf{b}$ -direction data for all three dopings suggests that the displacement pattern involves  $\mathbf{c}$  axis displacements of the bilayer oxygens, similar to those proposed for the soft phonon in  $\text{YBa}_2\text{Cu}_3\text{O}_7$  [18]. o-III and o-VIII show modulations along both  $\mathbf{a}$  and  $\mathbf{b}$  [1–3]. There are small differences between the values of the modulation periods for the  $\mathbf{a}$  and  $\mathbf{b}$  directions (Table 1) and in the patterns of atomic displacements, showing that the influence of the chains on the planes is also noticeable in o-VIII and o-III. If the two distortions develop independently, one would expect a different  $T_{\text{CDW}}$  for modulations along each direction, with the postulated  $2\text{-}\mathbf{q}$  state forming at lower temperatures. To date, we have no evidence for two different  $T_{\text{CDW}}$ 's in o-VIII or o-III. This is clearly not the case in o-II. The absence of a CDW along

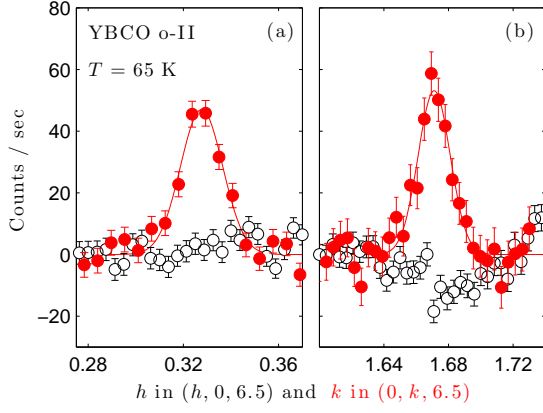


FIG. 2: (a)-(b)  $h$ - and  $k$ -scans, taken on o-II, through  $(|n - \delta_1|, 0, 6.5)$  and  $(0, |n - \delta_2|, 6.5)$  with  $n = 0, 2$  and  $T \sim T_c$ . The  $k$ -scans (red circles), showing lattice modulation peaks at  $(0, \delta_2, 6.5)$  and  $(0, 2 - \delta_2, 6.5)$ , are the same as displayed in Fig. 1(a,b). Equivalent measurements in the  $(h, 0, \ell)$ -plane (black circles) reveal no evidence for a lattice modulation at  $\delta_1 \sim \delta_2$ . A linear background has been subtracted from all scans.

**a** in this sample may reflect its simpler and more perfect oxygen-chain order (coherence length  $\xi_a > 200$  Å for o-II;  $\sim 50$  Å for o-III and  $\sim 30$  Å for o-VIII). This could result in more pronounced effects on the electronic band structure, which would include a chain Fermi surface with spanning vectors along  $\mathbf{b}^*$ , which might encourage CDW formation. Furthermore, the alternating filled and empty chains create an additional potential with a period of  $2a$  which may reduce the tendency for a CDW modulated along  $\mathbf{a}$ . If  $T_{\text{CDW}}$  along the  $\mathbf{a}$  direction is sufficiently below  $T_c$ , it might only appear if superconductivity is suppressed by a sufficiently large field.

An important issue in the cuprates is the relationship of the spin and charge correlations [1, 2, 9, 10]. In a simple stripe picture of intertwined spin and charge correlations [10], where the underlying antiferromagnetism (AF) and charge density have modulations characterised by wavevectors  $\delta_{\text{spin}}$  and  $\delta_{\text{charge}}$  respectively. These yield spin and charge peaks at positions  $\tau_{\text{AF}} \pm \delta_{\text{spin}}$  and  $\tau_{\text{lattice}} \pm \delta_{\text{charge}}$ , where  $\delta_{\text{charge}} = 2\delta_{\text{spin}}$ . This simple relationship appears to describe observations in  $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$  (see Fig. 4) and  $\text{La}_{1.6-x}\text{Nd}_{0.4}\text{Sr}_x\text{CuO}_4$  [9, 10]. In YBCO, the low-frequency spin fluctuations are anisotropic [20, 21], with the strongest response for  $\delta$  along  $\mathbf{a}^*$ . Indeed, lightly doped  $\text{YBa}_2\text{Cu}_3\text{O}_y$  shows magnetic order [19] with  $\delta$  along  $\mathbf{a}^*$ . Thus in YBCO (see Fig. 4), not only are  $\delta_{\text{spin}}$  and  $\delta_{\text{charge}}$  in different directions, but they show different trends and  $|\delta_{\text{charge}}| \neq 2|\delta_{\text{spin}}|$ . These differences suggest that  $\delta_{\text{spin}}$  and  $\delta_{\text{charge}}$  have different origins, e.g. they may be determined by different Fermi surface nesting vectors.

We may also consider  $T_{\text{CDW}}$  as a function of doping

(Table 1), although we stress the difficulty in determining unambiguously the onset of a small signal from a large background. In Fig. 3 (c), it is clear that for o-II, the CDW appears at a higher temperature, indicating that as the hole doping is reduced,  $T_{\text{CDW}}$  increases. This pattern coincides roughly with the onset of the polar Kerr effect [5] and the inflection point  $T_H$  below which the Hall coefficient begins to fall towards negative values [6], as suggested previously [2]. This indicates that all these measurements are sensitive to the same lattice symmetry breaking process.

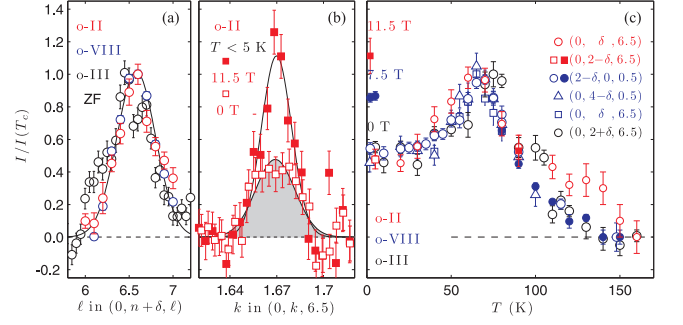


FIG. 3: Out-of-plane momentum  $\ell$ -, field- and temperature-dependence of the CDW modulation peaks found in YBCO o-II (red), o-VIII (blue) and o-III (black). All intensities have been background-subtracted and normalized to  $I(T_c)$  in zero field. (a)  $\ell$ -dependence of the peak height of  $k$ -scans through  $(0, n + \delta_2, \ell)$  with  $n = 0$  for o-II and o-VIII, and  $n = 2$  for o-III. All compounds show a broad peak centered at  $\ell \sim 6.5$  and a  $c$ -axis correlation length  $\xi_c$  comparable to that previously reported [2] in o-VIII at  $T = 2$  K for  $\ell = 0.5$ . (b) Measurement in a separate cryostat of the effect on CDW intensity in o-II of a magnetic field applied with a component 11.5 T along the  $c$ -axis of the crystal. (c) Temperature dependence of peak intensities, measured at the wave vectors indicated.

This places our observations in context with other low-field measurements. However, originally, the existence of CDW order was indicated by high-field NMR work on o-II [4]. This was revealed by a splitting, at high magnetic field and low temperature, of the NMR/NQR lines of the  $\text{Cu}2\text{F}$  sites, which lie in the  $\text{CuO}_2$  planes next to a filled  $\text{CuO}$  chain. This splitting was most simply explained by invoking a  $1\text{-}\mathbf{q}$  CDW along the  $\mathbf{a}$  direction with  $\delta = 0.25$  [22], which could give a  $\text{Cu}2\text{F}$  splitting, while having no effect on the  $\text{Cu}2\text{E}$  sites next to empty chains. However, very recent ultrasonic data [16] indicate that under similar high-field conditions o-II is actually  $2\text{-}\mathbf{q}$ . This is inferred from the sharp knee in velocity for the  $c_{66}$  shear mode seen at 18 T, which can only couple to a CDW having components of propagation and displacement in both directions in the  $\mathbf{a}\text{-}\mathbf{b}$  plane. Our present *zero-field* results show that o-II exhibits a CDW modulation vector different in magnitude and direction from that inferred from the NMR data, but similar to that seen by diffraction at other dopings [1–3]. Assuming

that the CDW is responsible for the FS reconstruction, the weak doping-dependence of QO frequencies [12, 13] also suggests that o-II develops CDW order similar to adjacent dopings. We are ineluctably driven to seek a new explanation for the NMR data consistent with these other measurements.

Firstly, we note that the onset fields and temperatures given by NMR [4] and ultrasonics [16] differ from those given by X-ray diffraction [1–3]. As discussed extensively elsewhere [1, 2], NMR (and ultrasonics) are relatively low-frequency techniques, and it seems likely that quasi-static CDWs become visible to X-rays before they become slow enough to have strong effects on NMR and ultrasonics. It is possible that the anomaly seen at 18 T with ultrasound [16] is the locking of the CDW order that we observe into  $\delta \rightarrow 1/3$ , and/or the appearance of an additional modulation along **a**.

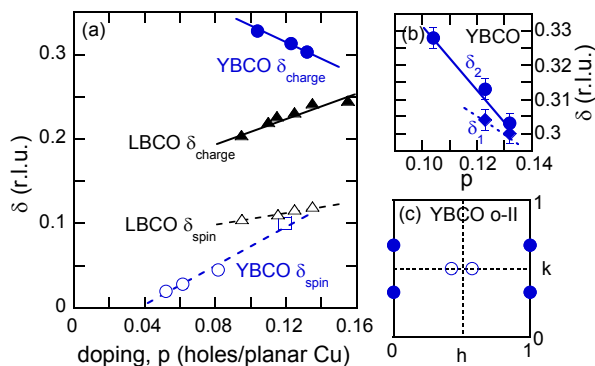


FIG. 4: (a) Spin and charge incommensurability versus doping for YBCO and  $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$  (LBCO). The spin incommensurability of both YBCO [19] and  $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$  [9] increases with doping. In LBCO the spin and charge incommensurability are simply related:  $\delta_c \approx 2\delta_s$ . In YBCO, the spin and charge incommensurability have opposite trends with doping. (b) The charge incommensurability in YBCO plotted on an expanded scale. (c) In YBCO o-II, the wavevectors of the spin ( $\delta_{\text{spin}}$ ) and charge ( $\delta_{\text{charge}}$ ) modulations are along different directions: the **a**- and **b**- axes respectively.

A  $1\text{-}\mathbf{q}$  incommensurate sinusoidal charge density wave along **b** would give a bimodal distribution of NMR/NQR frequencies at a given Cu site, with van Hove peaks at the extremal values, while a  $1\text{-}\mathbf{q}$  commensurate  $\delta = 1/3$  modulation can give two peaks of unequal weight. If barely-resolved, either could mimic a simple splitting. In contrast, a  $2\text{-}\mathbf{q}$  incommensurate pattern, with the two components identical, would give a single central van Hove peak. However, a  $2\text{-}\mathbf{q}$  pattern with one component having rather weaker effects than the other, could again give a bimodal distribution, similar to that observed for the  $\text{Cu}2\text{F}$  sites. A question for any modulation along **b** is to explain the much smaller effects of the CDW on the  $\text{Cu}2\text{E}$  sites. This could arise if the CDW caused larger displacements of the atoms (e.g. oxygen O3) near the

$\text{Cu}2\text{F}$  sites as is allowed by symmetry in the full o-II unit cell. Alternatively, the stronger effects of the CDW at the  $\text{Cu}2\text{F}$  sites may be related to their proximity to the conducting charge-reservoirs represented by the well-ordered Cu-O chains. We put forward this model in an attempt to reconcile apparently conflicting results from different methods. At present diffraction data cannot be taken at sufficiently high steady magnetic fields to provide structural data to complement the spectroscopic data from NMR, the thermodynamic data from ultrasonics and the Fermi surface data from QO.

In summary, we have detected CDW ordering in ortho-II YBCO in zero magnetic field. Within experimental sensitivity, the ordering has been found to be  $1\text{-}\mathbf{q}$ , with  $\mathbf{q}_{\text{CDW}}$  along the **b** (chain) direction. This contrasts with nearby higher dopings having less perfect Cu-O chain order, where  $2\text{-}\mathbf{q}$  structures are observed. The incommensurability and  $T$ -dependence of the CDW order are very similar to those previously reported in o-VIII and -III YBCO, but there is a clear trend to a larger  $q_{\text{CDW}}$  at lower doping; this suggests a band-structure influence on  $q_{\text{CDW}}$ . The observation in o-II YBCO of a  $1\text{-}\mathbf{q}$  charge modulation along **b** strongly suggests that a simple spin/charge stripe picture may not be appropriate, since the incipient spin correlations have a wavevector along **a**. The independent values of the spin and charge correlation  $\mathbf{q}$ -vectors over a range of dopings indicates that these have different origins in  $\text{YBa}_2\text{Cu}_3\text{O}_y$ . For YBCO o-II, the modulation direction in zero field and its incommensurability are completely different from those inferred from high-field NMR data. We propose an alternative explanation of these data in which an additional modulation appears at high magnetic fields.

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